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TECHNY, AL REPORT 3115

THE COMPATIBILITY OF ADVANCED PACKAGEABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

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OCTOBER 1983

AMCMS 5221.11.145.021

DA PROJECT \*5222901A203

PICATINNY ARSENAL DOVER, NEW JERSEY

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#### TECHNICAL REPORT 3115

FINAL REPORT.

THE COMPATIBILITY OF ADVANCED PACKAGEABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION,

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#### INTRODUCTION

The object of this investigation was to determine what materials of construction are compatible with the rocket propellants oblering trifluoride and Hydrazoid P for extended periods of time.

Certain Army missile propulsion needs can best bounded by prepackaged liquid rocket power plants. These combine the convenience of handling of solid rocket power plants with the higher energy, flexibility, and controllability of liquid propellants. The classic pair of storable and packageable propellants, UDMH and IRFNA, however, are inadequate for future applications, and more energetic combinations must be sought.

Such a combination is Chlorine Trifluoride (CTF) and Hydrazoid P. The latter is a low freezing hydrazine mixture designed for use with a pure halogen oxidizer. It consists of four moles of monomethyl hydrazine, five of hydrazine, and one of perchloric acid, combined, of course, with the hydrazines.

Before these propellants can be used in a missile system, it is necessar to determine their long-time compatibility with materials of construction, particularly those which may be used in tankage. As Army requirements demand storability at any temperature between -65 F and +160 F, compatibility studies should emphasize the behavior of the materials investigated at the latter temperature. Here the conditions are the severest that will be met in service, and tests continuing weeks can reveal weaknesse, that would not appear in years at room temperature. Thus, the two studies which comprise the body of this report emphasize the behavior of the propellants and the construction materials at the high temperature end of the storage

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It should be emphasized that these studies are directed at long time

storage. If it appears that Hydrazoid P, for instance, is incompatible with nickel over a period of weeks, this by no means implies that a nickel injector can not be used with this propellant. And if Teflon swells in contact with CTF, that does not mean that Teflon O-rings can not be used in the system plumbing, where they will be in contact with the propellant only for a time measured in seconds.

#### SUMMARY

A study has been made of the compatibility of various materials of construction with Hydrazoid P at room temperature and at 160°F, and with chlorine tri-fluoride at 160°C. The Hydrazoid P tests, which ran for 3600 hours, included the materials:

Stainless Steel	301	Inconel
	304	Nickel
	347	Tantalum
	17-7 PH	Titanium
Aluminum	2024	Polyethylene
	6061	Teflon
		Kel-F

The Chlorine trifluoride tests, which ran for 1728 hours, included the materials:

Stainless Steel	302	Aluminum	1100	Nickel
	304		2024	Copper
	316		5052	Inconel
	321		6061	Monel
	347		7075	Teflon.
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Corrosion was monitored by weight loss of the specimen tested and by examination of its surface.

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1. The aluminum alloys, tantalum, titanium, polyethylene, and Teflon were unaffected by Hydrazoid P. The Inconel, nickel, and the stainless steels were appreciably corroded and the propellant was contaminated by corrosion products. The Kel-F swelled and blistered.

2. None of the materials tested were appreciably corroded by ehlorine trifluoride.

#### RECOMMENDATIONS

-1. Aluminum and titanium are recommended for tank materials for Hydrazoid P, and polyethylene and Teflon for O-ring material.

-3. Both aluminum and stainless steel can be recommended as tank materials for chloring trifluoride. Teflon is the only non-metallic O-ring material recommended.

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#### COMPATIBILITY STUDIES

#### Chlorine Trifluoride

The corrosivity of chlorine trifluoride (CTF), and its compatibility with materials of construction at room temperatures is quite well known but there is little information available as to its corrosive behavior at 70 to 80°C, (Reference 1). (In the region of the 160°F Mil. Spec. limit.) This study was intended to remedy, to some extent, this situation. The materials put under test were those which are compatible with CTF at room temperature and which might be expected to be so at 160°F. They include:

Stainless Steel	302	Aluminum	1100	Nickel
	304		2024	Copper
	316		5052	Inconel
	321		6061	Monel
	347		7075	Tellon
			2 <b>-</b> S	

Kel-F was not tested because ambient temperature tests showed that it absorbed CTF which could not be removed by baking at 100°C.

The samples were in the form of thin strips approximately 3.2 cm x 1.3 cm and were exposed to the CTF in sealed SS cylinders (Figure 1) in a water bath held at 70-80 C. The CTF was used as received. It was nominally 99 percent pure, the major impurity being HF. Periodically, the samples were removed, examined, dried, and weighed. The average weight loss after 1728

hours is listed in Table 1, in milligrams per square centimeter of exposed surface, as is the average rate of corrosion, in mils per year.

The comparatively high corrosion rate of the SS 316 is attributed to the fact that the test cylinder containing it ruptured during the last test period, and some water was presumably picked up to increase the corrosion by the formation of HF.

The Teflon samples were exposed to the CTF at  $160^{\circ}$  F for 312 hours and absorbed approximately 1.5 weight per int of CTF. This was almost completely driven off when the samples were baked at  $100^{\circ}$  C. There was no other discoverable effect on the Teflon.

It can be concluded that all of the metals tested, as well as Teflon, are satisfactory for long time service with CTF, since even at  $160^{\circ}$ F the corresion rate is negligible for all practical purposes.

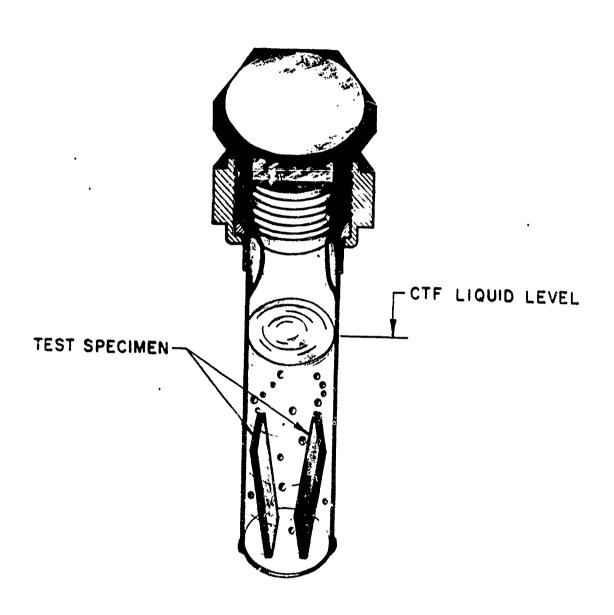


Fig 1. STAINLESS STEEL CTF COMPATIBILITY CYLINDER

TABLE 1: CORROSION IN CTF AT 160° F, 1728 HOURS.

SS 302	mg/cm <sup>2</sup> 0. 23	Mils/yr 0.05	
SS 316	1. 60	0. 41	
SS 304	0.35	0.09	
SS 321	0. 14	0.04	
SS 347	0. 23	0.06	
Al 1100	0.69	0. 51	
A1 2024	0.05	0, 03	
A1 5052	0. 10	0, 08	
A1 6061	0, 08	0.06	
A1 7075	0.12	0.09	
A1 25	0.05	0.04	
Nickel	0.55	0.12	
Copper	0.71	0. 16	
Monel	0. 28	0. 11	(968 Hrs)
Inconel	0.14	0.05	(832 Hrs)

#### Hydrazoid P

Data on the corrosivity of Hydrazoid P and its compatibility with materials of construction has hitherto been lacking. The purpose of this study is to remedy this lack. The materials studied were those which were known to be compatible with hydrazine and might reasonably be expected to be compatible with Hydrazoid P, (Reference 2) They include:

Stainless Steel	301	Inconel
	304	Nickel
	347	Tantalum
	17-7 PH	Titanium
Aluminum	2024	Polyethylene
	6061	Kel-F
		Teflon

The samples were in the form of carefully cleaned thin strips, 3.9 x 2.2 cm, and were exposed to the Hydrazoid P in sealed glass flasks (Figure 2) at room temperature and in a water bath held at  $70-72^{\circ}$  C (158-162°F). The Hydrazoid P was made up in this laboratory, and assayed as follows:

Monomethyl Hydrazine	$\mathrm{CH_3N_2H_3}$	39.0%
Hydrazine	N <sub>2</sub> H <sub>4</sub>	37.6%
Perchloric Acid	HClO <sub>4</sub>	22.9%

The tests were continued for 150 days (3600 hours). Triplicate samples of each material were exposed. Periodically, they were removed from the test containers, washed, dried, examined, and weighed.

AA6081, AA2024, Titanium, Tantalum, Polyethylene, and Teflon were completely unaffected by the propellant in 150 days, at room temperature and at 160 °F. There was no observable weight change (less than 0. 1mg) and no visible change of any sort, and these materials can be considered as completely compatible with Hydrazoid P and suitable for unlimited service with this propellant.

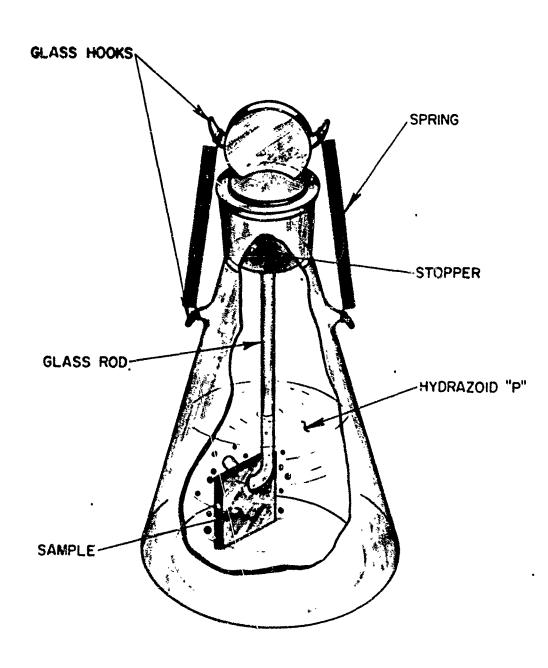


Fig 2. HYDRAZOID P COMPATIBILITY TEST

At 160°F, Kel-F turned dark brown, after ten days, but there was no othe observable change for the first 120 days except a slight increase in weight. Shortly thereafter the sample began to lose weight, its surface became pimpled and the propellant started to turn brown. The weight loss continued until the end of the test. A photomicrograph of the test sample after 150 days is shown in Figure 3. A similar, but much less marked effect wa noticed at room temperature. This attack upon Kel-F is reminiscent of a unilar effect noticed some ten years ago at Pt. Mugu, where Kel-F sheet incended for expulsion bags was completely disintegrated by aniline.

The nickel, the Inconel, and the four stainless steels were attacked by the propellant. The 150 day results are shown in Table 2, where the average corrosion is shown as mg/cm<sup>2</sup> per 150 days, and, assuming a constant, average corrosion rate, as mils/year.

The propellant was discolored, acquiring a pinkish-purple hue, whose intensity varied, naturally, with the extent of the corrosion. This is apparently due to the formation of a cation  $Ni(N_2H_4)_X^{1+}$  such as those reported by Kramer, (Reference 3). This cation is apparently a very strong base, since analysis of the propellant arting upon the nickel at  $160^{\circ}$  F, showed that in two weeks the apparent perchloric acid content had dropped by two percent. It appears probable that the high temperature corrosion of the nickel would have been considerably larger at the 150 day mark were it not for the depletion of the perchloric acid and the accumulation of corrosion products in the solution.

Photomicrographs of the nickel and Inconel specimens after 150 days at 160°F are shown in Figures 4 and 5.

It is apparent that neither nickel nor alloys containing considerable percentages of that metal are suitable container materials for the long-time storage of Hydrazoid P.

At 160°F, Kel-F turned dark brown, after ten days, but there was no other observable change for the first 120 days except a slight increase in weight. Shortly thereafter the sample began to lose weight, its surface became pimpled and the propellant started to turn brown. The weight loss continued until the end of the test. A photomicrograph of the test sample after 150 days is shown in Figure 3. A similar, but much less marked effect wa noticed at room temperature. This attack upon Kel-F is reminiscent of a milar effect noticed some ten years ago at Pt. Mugu, where Kel-F sheet intended for expulsion bags was completely disintegrated by aniline.

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It is apparent that neither nickel nor alloys containing considerable percentages of that metal are suitable container materials for the long-time storage of Hydrazoid P.

TABLE 2: CORROSION IN HYDRAZOID P, 3600 HOURS.

	Ambient Temperature		160° F	
	mg/cm <sup>2</sup>	Mils/yr	mg/cm <sup>2</sup>	Mils/yr
Nickel	10. 58	1. 07	24.74	2. 43
Inconel	6. 98	0.81	13, 73	1. 40
SS 304	0.67	0. 053	18.81	1. 38
SS 301	0.58	0.042	10, 15	0.79
SS 347	0. 13	0.010	6. 52	0. 50
17-7 PH	0.72	0.046	6. 52	0. 42

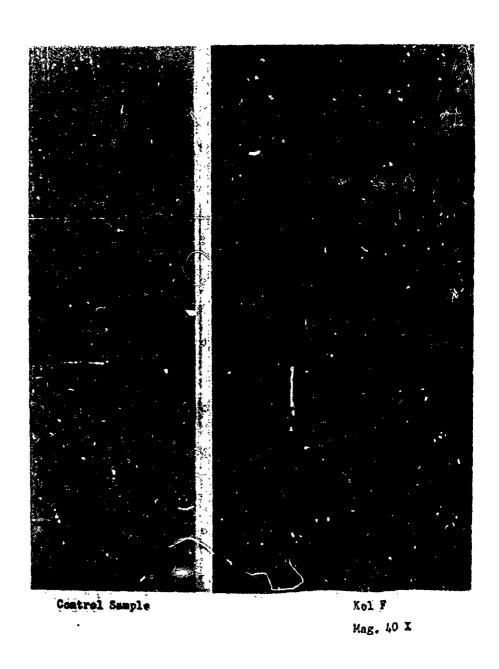


Fig 3. KEL-F AFTER 150 DAYS IN HYDRAZOID P AT 160° F

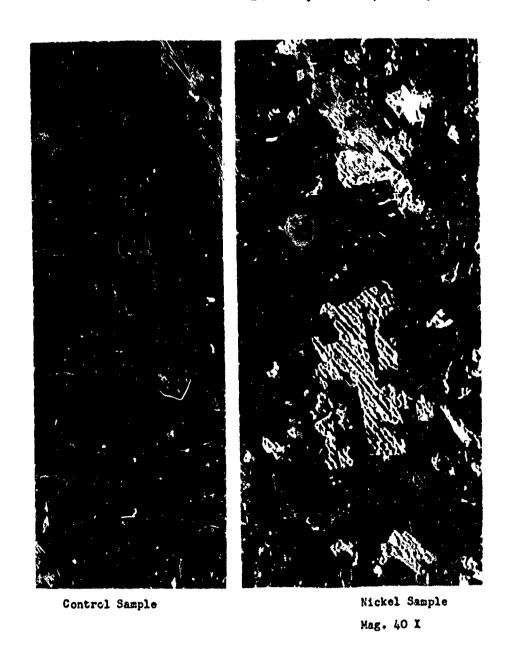


Fig 4. MICKEL AFTER 150 DAYS IN HYDRAZOID P AT  $160^{\circ}\,\mathrm{F}$ 

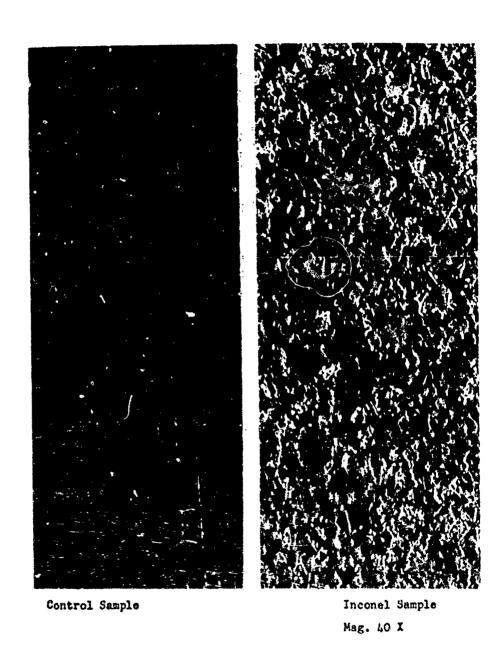


Fig 5, INCONEL AFTER 1:0 DAYS IN HYDRAZOLD P AT 160°F

#### REFERENCES

- l. <u>Compatibility of CTF with Materials of Construction</u>, Pennsalt Chemicals Corp., April 1961.
- 2. Hydrazine Handling Manual, Rocketdyne, R-3134, Sept 1961.
- 3. G. M. Kramer et al. <u>The Effect of Various Materials upon the Stability of the Hydrazine Hydrazine Nitrate Water System</u>, Frankford Arsenal, R-1100, Sept 1952.

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Liquid Propellant
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Boyce, A. E.
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Compatibility

Package

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Propellant

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